The Selective Photooxidation of Methane and Ethane with Oxygen over Zinc Oxide and Molybdena-loaded Zinc Oxide Catalysts

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The photoinduced oxidation of methane or ethane over zinc oxide based catalysts under UV irradiation at 500–550 K gives formaldehyde with high selectivity or acetaldehyde, respectively.

Direct conversion of methane into oxygen-containing chemicals under mild conditions is of current interest.[1] We have reported the first example of selective photooxidation of methane into formaldehyde, which was attained on silica supported molybdena above 440 K.[2] Photocatalytic oxidation of alkanes on solid semiconductors, such as TiO_2 or ZnO, has been studied by many investigators.[3,4] However, only a few reports have dealt with the catalytic ability to induce photooxidation of methane, and most of these studies resulted in deep oxidation.[5]

In the present communication, we report the photoinduced selective conversion of methane into formaldehyde using molybdena-loaded zinc oxide catalysts in the presence of oxygen at 500–550 K. The photooxidation of ethane into acetaldehyde is also reported.

The MoO_3-loaded ZnO catalyst was prepared by the usual impregnation method with an aqueous solution of ammonium heptamolybdate. The catalyst was calcined in air at 823 K for 2 h *in situ*. The reaction was then carried out, typically for 2 h for oxidation of methane and 1 h for that of ethane, in a fixed bed flow type quartz reactor, which has a window for UV irradiation (11 × 20 mm; inner thickness 1 mm), equipped with a quartz tube to cover the whole reactor tube. The temperature of the catalyst bed was controlled by passing heated air around the reactor. A high-pressure mercury vapour lamp (200 W, arc length 75 mm) was used for UV irradiation. Liquid products from oxidation of methane and

Table 1 Photooxidation of methane over ZnO-based catalysts[a]

		Yield/μmol h^{-1}			
Run	Catalyst	HCHO	MeOH	CO	CO_2
1	ZnO	3.1	0.4	4	27
2[b]	ZnO	2.5	0.5	trace	23
3[c]	ZnO	n.d.	n.d.	n.d.	n.d.
4	MoO_3(5 wt.%)/ZnO	4.8	0.1	n.d.	1
5[b]	MoO_3(5 wt.%)/ZnO	4.0	0.1	n.d.	n.d.
6[c]	MoO_3(5 wt.%)/ZnO	n.d.	n.d.	n.d.	n.d.

[a] Amount of catalyst = 0.25 g, methane feed rate = 7.5 mmol h^{-1}, $CH_4:O_2:He = 3:1:10$, W/F = 7.1 g h mol^{-1}, n.d. = not detected, temperature of the catalyst bed = 493 K. [b] Irradiated through a Pyrex filter. [c] Without UV irradiation, temperature of the catalyst bed = 548 K.

Table 2 Photooxidation of ethane over ZnO-based catalysts[a]

		Yield/μmol h^{-1}				
Run	Catalyst	MeCHO	EtOH	HCHO	CO	CO_2
7	ZnO	86	3.4	5	8	61
8[b]	ZnO	88	3.4	5	7	63
9[c]	ZnO	64	2.1	7	3	38
10[d]	ZnO	n.d.	n.d.	n.d.	n.d.	n.d.
11[e]	ZnO	5.2	n.d.	n.d.	n.d.	7
12	MoO_3(5 wt.%)/ZnO	14	trace	5	n.d.	8
13[c]	MoO_3(5 wt.%)/ZnO	11	n.d.	3	n.d.	5
14[d]	MoO_3(5 wt.%)/ZnO	n.d.	n.d.	n.d.	n.d.	n.d.

[a] Amount of catalyst = 0.25 g, ethane feed rate = 7.5 mmol h^{-1}, $C_2H_6:O_2:He$ = 3:1:10, W/F = 7.1 g h mol^{-1}, n.d. = not detected, temperature of the catalyst bed = 493 K. [b] Values obtained in the prolonged run of 4–5 h. [c] Irradiated through a Pyrex filter. [d] Without UV irradiation. [e] Temperature of the catalyst bed = 340 K.

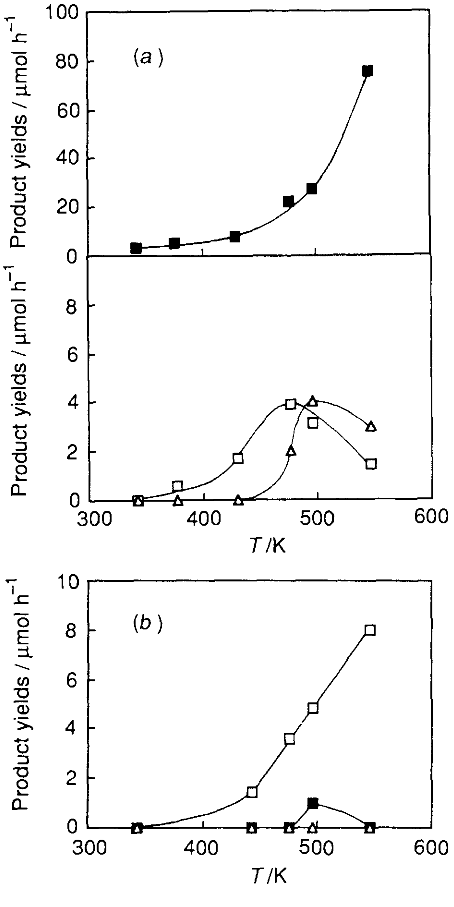

Fig. 1 The product yields at various catalyst bed temperatures over (*a*) ZnO and (*b*) MoO_3(5 wt.%)/ZnO catalysts. The yields of (□) HCHO, (△) CO and (■) CO_2.

from that of ethane were collected in an ice–water trap at 273 K and a solid carbon dioxide-acetone trap at 195 K, respectively. Products were analysed by gas chromatography using thermal conductivity and flame ionisation detectors (detection limit; carbon oxides ~ 0.002 vol.%, aldehydes and alcohols ~ 0.1 μmol).

The results of photooxidation of methane are shown in Table 1. The ZnO catalyst afforded 3.1 μmol h^{-1} of formaldehyde and a large amount of CO_2, 27 μmol h^{-1} along with small amounts of methanol, CO and H_2. The selectivity for formaldehyde was *ca.* 9% and that of CO_2 was over 70%. As shown in runs 3 and 6, UV irradiation was indispensable for the formaldehyde formation. The addition of 5 wt.% of MoO_3 to ZnO catalyst suppressed the formation of CO_2, CO and H_2 almost completely, whereas the yield of formaldehyde increased to 4.8 μmol h^{-1}. The reactions under UV irradiation through the Pyrex filter suggest that a wavelength longer than 300 nm is able to activate both ZnO and MoO_3/ZnO catalysts (see runs 2 and 5). This is in good contrast to the result that the MoO_3/SiO_2 catalyst requires a wavelength shorter than 300 nm to form formaldehyde.[2]

Fig. 1 shows the changes in the product yields with variations in the catalyst bed temperature. Elevated temperatures were required for formaldehyde formation with both ZnO and MoO_3/ZnO catalysts. With the ZnO catalyst, the formaldehyde and CO yields showed maximum values of 3.9 μmol h^{-1} at 473 K and 4 μmol h^{-1} at 493 K, respectively. By contrast, the yield of CO_2 increased monotonically with increase in the catalyst bed temperature. However, with the MoO_3/ZnO catalyst, the formaldehyde yield increased markedly with temperature up to 548 K. The yields of carbon oxides did not exceed 1 μmol h^{-1}. At 548 K, 8.0 μmol h^{-1} of formaldehyde was selectively formed with 0.2 μmol h^{-1} of methanol.

Table 2 shows the results of the photooxidation of ethane. The products were acetaldehyde, ethanol, formaldehyde, CO_2 and small amounts of ethene, CO and H_2. With ZnO catalyst, 86 μmol h^{-1} of acetaldehyde (1.1% of ethane feed) was formed together with 61 μmol h^{-1} of CO_2. The product yields did not change during a prolonged run for 5 h (run 8). A decrease in the product yields on UV irradiation through a Pyrex filter was observed, as in the oxidation of methane. Without UV irradiation, reactions were not detectable (runs 10 and 14). Without heating the catalyst bed, the product yields markedly decreased (run 11). In contrast with the photooxidation of methane, the addition of MoO_3 to ZnO decreased both the yields of acetaldehyde and CO_2 to 14 and 8 μmol h^{-1}, respectively.

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